

CRYSTALLOCHEMICAL AND MAGNETIC BEHAVIOUR OF Sc(FeAl)₁₂ SAMPLES BY POWDER DIFFRACTION AND MÖSSBAUER TECHNIQUES

K. REĆKO¹, K. SZYMAŃSKI¹, L. DOBRZYŃSKI^{1,2}, D. SATULA¹,
B. C. HAUBACK³, W. SUSKI^{4,5}, B. YU. KOTUR⁶

¹*Institute of Experimental Physics, University of Białystok,
Lipowa 41, 15-424 Białystok, Poland*

²*The Soltan Institute for Nuclear Studies,
05-400 Otwock-Świerk, Poland*

³*Department of Physics, Institute for Energy Technology,
P.O. Box 40, N-2027 Kjeller, Norway*

⁴*Polish Academy of Sciences, W. Trzebiatowski Institute of Low Temperature and Structure Research,
P.O. Box 1410, 50-950 Wrocław 2, Poland*

⁵*International Laboratory of High Magnetic Fields and Low Temperatures,
Gajowicka 95, 53-421 Wrocław, Poland*

⁶*Department of Inorganic Chemistry, L'viv State University,
bul. Kirila i Mefodiya 6, L'viv 290005, Ukraine*

Abstract: Chemical ordering and magnetic properties of ScFe₄Al₈, ScFe₅Al₇ and ScFe₆Al₆ powder samples are presented. These alloys have been measured by means of powder diffraction techniques, namely X-ray and thermal neutron one, conventional Mössbauer effect (ME) method as well as by Monochromatic Circularly Polarized Mössbauer Source (MCPMS). X-ray and neutron powder patterns allowed to determine crystallochemical structure of Sc(FeAl)₁₂ alloys with symmetry *I4mmm*, isostructural with ThMn₁₂-type of structure. The structure refinement in the paramagnetic state confirms the preference of the iron atoms for (*8f*) positions. For the ScFe₄Al₈ compound the iron site splits into two independent orbits under the action of the in-plane wave vector $q = (q_x, q_x, 0)$, where q_x has at 8 K the value 0.136(2) r.l.u. This Sc alloy orders around 250 K by forming antiferromagnetic spiral iron sublattice within the tetragonal basis plane *ab* while the scandium alloys with higher iron concentration exhibit ferromagnetic nature. The obtained results are discussed in relation to the (U, Th)(FeAl)₁₂ samples.

1. INTRODUCTION

Our earlier studies carried out on crystal and magnetic structures of (U, Th)(FeAl)₁₂ intermetallic compounds [1-2] indicated large crystallochemical similarity in both series of actinide's alloys. In the case of scandium samples this rule was broken. The latter turned out to exhibit new type of precipitations appearing during annealing procedure as well as a new kind of disordering within their lattices. All scandium compounds were found to contain non-overlapping peaks of an until now unknown impurity phase which disclosed much lower symmetry than the ones, mainly cubic FeAl-type, appearing in U- or Th-samples. In addition, the *a-f* disordering in the basic phase was observed which contrasts with previously investigated samples where typically *f-j* disordering took place.

On the magnetic side, with increasing iron content the isostructural UFe_xAl_{12-x} alloys [1-2] exhibited the transition from spin-canted system for $x = 4$, with the antiferromagnetic interactions

as a dominant ones, to the ferromagnetic ordering for $x = 6$. In the case of ThFe_4Al_8 sample in which only iron atoms were responsible for magnetism, the incommensurate magnetic structure was discovered [3]. The same situation was found in scandium sample with $x = 4$. We note that the magnetic behaviour of ScFe_4Al_8 raised already some controversies in the literature [4-5]. The published results indicated presence of a spin glass state or a mixture of antiferromagnetic structure and spin glass. Our unpolarized neutron diffraction pattern, however, leaves no doubts that the modulated magnetic structure is observed in the ScFe_4Al_8 compound. In fact this compound has long-range magnetic order in the iron sublattice while the Sc-Sc interaction is negligible.

2. EXPERIMENTAL DETAILS

All scandium samples with iron concentration $x = 4, 5$ and 6 were prepared by arc-melting in the Department of Inorganic Chemistry, L'viv State University (Ukraine). Arc melting of the stoichiometric quantities of the components under the protective argon atmosphere was applied for preliminary reaction. This procedure was followed by homogenization during 8 weeks at about 875 K. The lumps obtained were next crushed into a powder and underwent prolonged annealing at about 1075 K for week likeness to identical preparation of previously investigated (U, Th)(FeAl)₁₂ intermetallics. The neutron experiments have been performed at Department of Physics, Institute for Energy Technology, Kjeller (Norway). The high resolution powder diffractometer PUS ($\lambda = 155.02$ pm) was used for crystal and magnetic structure determination in the temperature range 8-300 K. The X-ray measurements were carried out on the HZG-4C diffractometer installed in the Institute of Experimental Physics in Białystok. The standard wavelengths used at RT were 154.06 and 178.82 pm. The Mössbauer measurements were also carried out in Białystok. The ⁵⁷Fe ME results were obtained using a constant-acceleration mode spectrometer with ⁵⁷Co source in a Rh matrix. The ⁵⁷Fe MCPMS measurements were carried out using ⁵⁷Co source in a Cr matrix. The filter technique was applied to absorb-out resonant photons with one polarisation [6]. The samples were cooled down to 12 K in the field of 1 T.

2. RESULTS

The X-ray and neutron powder diagrams show well ordered compounds with crystal structure characterized by Sc position (2*a*), Fe – (8*f*), Al – (8*i*) and mixed one Fe/Al – (8*j*) according to sample composition in the scandium alloys with higher iron content. The presence of low symmetry impurities were found for these latters. Contrary to previously measured uranium and thorium samples [1-7] the account of most probable so far FeAl (*Pm3m*) phase as well as metal oxides was excluded. The extra phase crystallizes during annealing process of $\text{ScFe}_x\text{Al}_{12-x}$ compounds exhibits crystal symmetry lower than all known by us $\text{Fe}_{1-x}\text{Sc}_x$ structures. The simulations of X-ray spectra allowed us to reject the hypothesis of the presence of basic systems superstructure. Due to small shortage (up to 5% per scandium site) the Fe/Sc disordering were disclosed for this family by diffraction techniques. The stoichiometry of $\text{ScFe}_x\text{Al}_{12-x}$ samples before and after annealing process (at 1075 K per one week) were as follow:

Before annealing	After annealing
$\text{Sc}_{1-\delta}\text{Fe}_4\text{Al}_{8-\delta}$, $\delta = 0.04$	$\text{Sc}_{1-\delta}\text{Fe}_{4-3\delta}\text{Al}_8$, $\delta = 0.05$
$\text{Sc}_{1-\delta}\text{Fe}_5\text{Al}_{7-\delta}$, $\delta = 0.08$	$\text{Sc}_{1-\delta}\text{Fe}_5\text{Al}_{7-3\delta}$, $\delta = 0.09$
$\text{Sc}_{1-\delta}\text{Fe}_{6-2\delta}\text{Al}_6$, $\delta = 0.03$	$\text{Sc}_{1-3\delta}\text{Fe}_{6-4\delta}\text{Al}_6$, $\delta = 0.03$

The largest impurity contribution to the observed integrated intensities ($\sim 15\%$) was found for ScFe_6Al_6 alloy and neglectable (less than 5%) for ScFe_4Al_8 one.

4. MAGNETIC PROPERTIES

The scandium atoms similarly to nonmagnetic thorium or uranium atoms occupy $(2a)$ positions in the system, so we can expect similar magnetic unit cell. Lack of uranium moment face very small or neglectable scandium magnetic moment should essentially decrease the crystal anisotropy. Special attention was dedicated to the homogeneity and magnetic behaviour of ScFe_4Al_8 , the magnetic structure of which raised some controversies [4-5, 7]. According to Authors [7] scandium itself does not order magnetically even at the temperatures as low as 0.1 mK, thus one can be used in non-magnetic reference compound in order to determine the contribution of the f -electron elements to the magnetism of intermetallic of our interest. The interpretation of the neutron data requires presence of non-zero magnetic propagation vector different from the nuclear one. The low-temperature pattern of ScFe_4Al_8 (Fig. 1) show the appearance of magnetic peaks in the form of weak satellites at temperatures below 250 K around nuclear reflections.

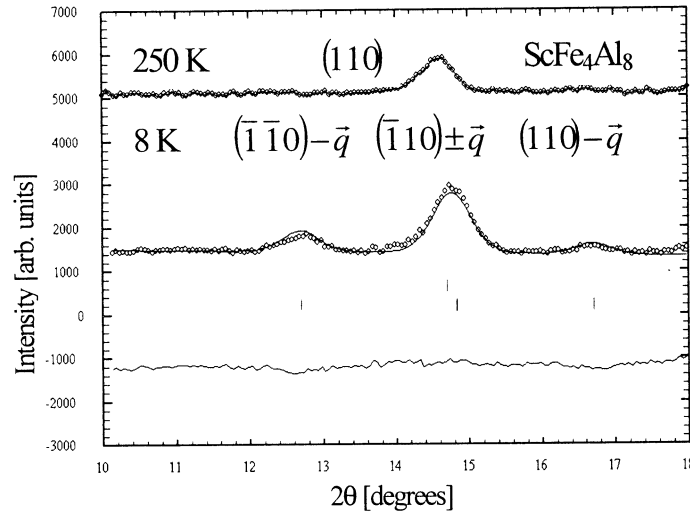


Fig. 1. Measured neutron diagrams at 8 K and 250 K, and for 8 K calculated and difference one. The indexing $(hkl) \pm \vec{q}$ with $\vec{q} = (q_x, q_y, 0)$ refers to the magnetic satellites present in all patterns up to T_N of ScFe_4Al_8 sample

The iron magnetic moments of ScFe_4Al_8 sample create spiral structure (cycloidal spiral) with spins rotated in a plane parallel to the wave vector $q = (q_x, q_x, 0)$, with $q_x = 0.136(2)$ which is temperature independent up to 175 K. The value of iron magnetic moment at 8 K is close to $1.08(12) \mu_B$. The basic magnetic cell has to be purely antiferromagnetic with iron spins directed along a or b axis and rotated in the basal plane by $49(1)^\circ$ from cell to cell (Fig. 2).

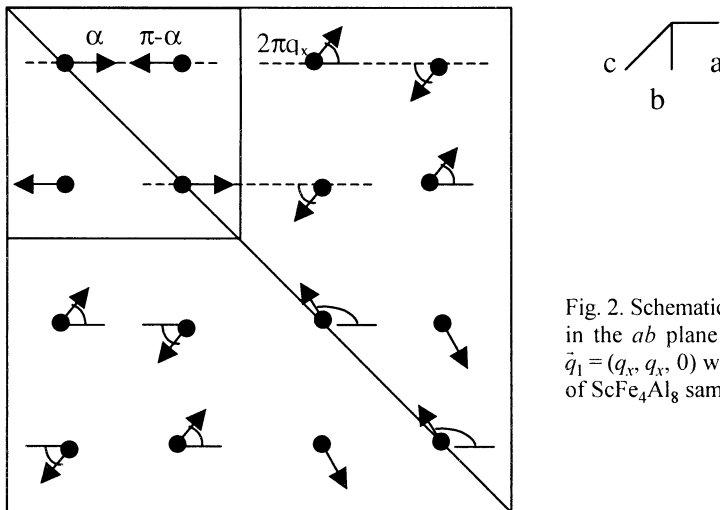


Fig. 2. Schematic distribution of the $\text{Fe}(f)$ spins in the ab plane according to magnetic vector $\vec{q}_1 = (q_x, q_x, 0)$ with $q_x > 0.125$ for the four cells of ScFe_4Al_8 sample

The antiferromagnetic nature of ScFe_4Al_8 is fully confirmed by Mössbauer measurements.

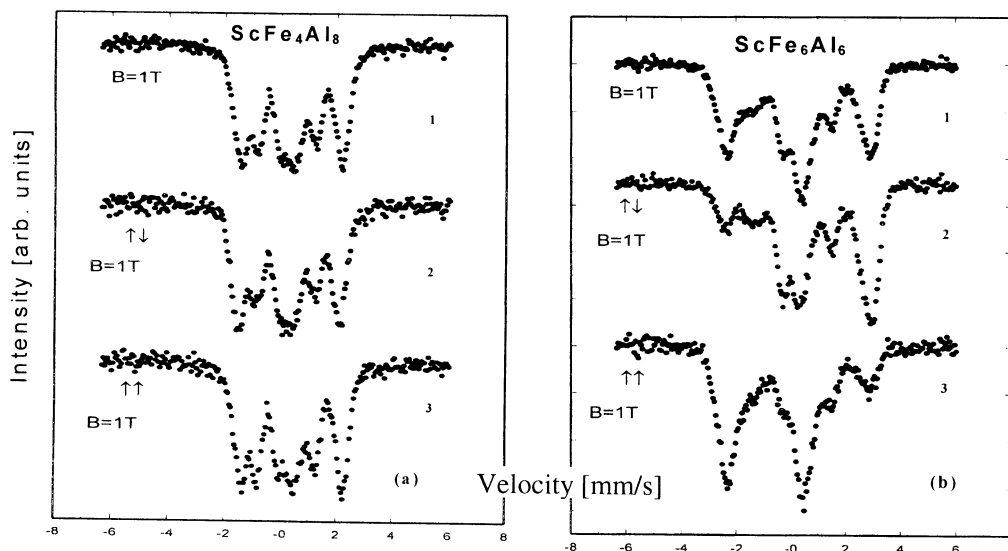


Fig. 3. Mössbauer spectra ScFe_4Al_8 (a) and ScFe_6Al_6 (b) measured with ME – 1 and with MCPMS for two polarizations: laevorotatory – 2 and dextrorotatory – 3

All Mössbauer spectra were measured at the magnetic field of 1 T. The magnetic spectra's components in the ME and MCPMS diagrams for ScFe₄Al₈ show that the angular distribution of iron magnetic moments is independent of the external magnetic field. This is typical for antiferromagnetically ordered sample. In contrast to that, the MCPMS spectra measured for ScFe₆Al₆ show that the angular distribution of iron magnetic moments is strongly dependent on the magnetic field that proves in turn a ferromagnetic nature of this alloy. The hyperfine magnetic field of ScFe₄Al₈ is equal to 11.20(2) T, very close to 11.5(3) T and 11.0(2) T obtained for ThFe₄Al₈ [3] and UFe₄Al₈ [1-2], respectively. The iron magnetic moment in the 1 T field reaches value of 1.24(8) μ_B at 12 K.

Because neither scandium nor thorium bear magnetic moments in the samples of our interest, the iron atoms must play key role in formation of the incommensurate magnetic structures in both, scandium and thorium alloys. In the case of uranium samples, the uranium itself is active ion formation of the magnetic structure, so one faces the necessity of explanation of all additional magnetic interactions, including anisotropic ones.

References

- [1] K. Rećko, K. Szymański, L. Dobrzyński, J. Waliszewski, D. Satuła, M. Biernacka, K. Perzyńska, W. Suski, K. Wochowski, A. Hoser, G. André, F. Bourée, J. Alloys Comp. **323-324**, 531 (2001).
- [2] K. Rećko, K. Szymański, L. Dobrzyński, D. Satuła, W. Suski, K. Wochowski, G. André, F. Bourée, A. Hoser, J. Alloys Comp. **334**, 1-2, 58 (2002).
- [3] K. Rećko, L. Dobrzyński, K. Szymański, D. Satuła, K. Perzyńska, M. Biernacka, J. Waliszewski, P. Zaleski, W. Suski, K. Wochowski, M. Hofmann, D. Hohlwein, Phys. Stat. Sol. (a) **196**, 344 (2003).
- [4] B. Yu. Kotur, D. Badurski, W. Suski, K. Wochowski, A. Gilewski, T. Mydlarz, Physica **B254**, 107 (1998).
- [5] P. Gaczyński, F. G. Vagizov, W. Suski, B. Yu. Kotur, W. Iwasieczko, H. Drulis, J. Magn. Magn. Mater. **225**, 351 (2001).
- [6] K. Szymański, L. Dobrzyński, B. Prus, M. J. Cooper, Nucl. Instrum. Methods, **B119** 438 (1996).
- [7] Y. Koika, H. Suzuki, J. Low Temp. Phys. **107**, 197 (1997).